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(21) International Application Number: PCT/US89/03793 (22) International Filing Date: 1 September 1989 (01.09.89) (71) Applicant (for all designated States except US): THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventor; and (75) Inventor/Applicant (for US only) : MOROHASHI, Masayuki [JP/JP]; Higashi Tanaka 702-B, Gotenba-shi, Shizuoka-ken (JP). (74) Agent: FIFIELD, David, H.; The Dow Chemical Company, P.O. Box 1967, Midland, MI 48641-1967 (US).		(81) Designated States: AU, BR, JP, SU, US. Published <i>With international search report.</i>
(54) Title: PROCESS FOR PURIFYING SUGAR SOLUTIONS (57) Abstract A sugar solution is purified by a process for purifying a sugar solution using a cation exchange resin and an anion exchange resin, which comprises contacting a sugar solution with a decolorization resin to remove color bodies and weakly acidic substances prior to the decationization by the cation exchange resin. The present invention is preferably used for purifying a solution of corn syrup, cane sugar, sorbitol, sucrose, dextrose or the like.		

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PROCESS FOR PURIFYING SUGAR SOLUTIONS

5 The present invention relates to a process for purifying a sugar solution containing a saccharide such as glucose, sorbitol, sucrose, xylose, ribose, inositol or isomerized sugar, at a high efficiency.

10 A sugar solution or liquor containing a saccharide such as glucose, isomerized sugar, cane sugar or sugar alcohol contains color bodies, salts, organic acids and the like as impurities. In the conventional process for purifying such sugar solutions, decolorization is accomplished by adsorbing color bodies
15 by activated carbon, and then salts and organic acids are removed by an ion exchange resin.

20 Activated carbon is not suitable for continuously decolorizing a large quantity of a sugar solution. Regeneration of the activated carbon is difficult. Moreover, the activated carbon decolorization process is disadvantageous because propagation of bacteria readily occurs. This makes it

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impossible to perform a continuous operation over a long period.

5 It is known that ion exchange resins can be employed as decolorization resins. For example, U.S. Patent 3,122,456 discloses a method of purifying and decolorizing sugar solutions with spongy cation exchanger resins permeated by small cavities or veins. U.S. Patent 2,578,938 teaches decolorizing sucrose
10 solutions with a mixture of a strongly basic anion exchange resin and a cation exchange resin. U.S. Patent 4,193,817 discloses the decolorization of sugar solutions employing chloride form of Type-1 strong-base anion exchange resin. Unfortunately, these processes
15 disclosed in the prior art are not sufficient to effectively remove all undesirable impurities such as color bodies and weak acids or weakly acidic substances from a sugar solution. The decolorizing action of a
20 decolorization resin is described, for example, in "Decolorization and Deodorization Using Ion Exchangers" (Chemical Factory, Volume 8 No. 5, pages 83 through 87).

25 It would be desirable to provide a process for removing substantially all of the undesirable impurities using ion exchange resins from a sugar solution at a high efficiency.

30 The present invention is a process for purifying a sugar solution using a cation exchange resin and an anion exchange resin, which comprises contacting a sugar solution with a decolorization resin to remove color bodies and weakly acidic substances prior to the decantionization by the cation exchange resin.

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The decolorization resins used in the invention absorb and remove not only color bodies but also weak acids or weakly acidic substances that reduce the efficiency of the ion exchange step.

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At the ion exchange step, in general, the ion exchange treatment is controlled by monitoring electroconductivity of a sugar solution which has passed through an anion exchange resin. More specifically, when such electroconductivity reaches a prescribed point (break through point), the ion exchange treatment is terminated. A strong acid is much more easily adsorbed in an anion exchange resin than a weak acid, and the weak acid passes through the anion exchange resin more rapidly than the strong acid. This means that if a weak acid is not removed from the sugar solution, the electroconductivity of the sugar solution rises more rapidly, i.e., the break through point is reached more rapidly resulting in a smaller quantity of treated solution. A weak acid in an aqueous solution which has passed through a cation exchange resin is not likely to be ionized due to a low pH of such solution. Thus, if the decolorization resin is placed between the cation exchange resin and the anion exchange resin, it is difficult to remove the weak acid at the decolorizing step. Therefore, a key element of the process of the present invention is contacting the sugar solution with the decolorization resin before the ion exchange step.

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Figure 1 shows the relationship between the time of the treatment of a glucose solution and the electroconductivity, as observed in the examples and comparative examples.

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The decolorization resin used in the present invention include, for example, anion exchange resins such as a strongly basic anion exchange resin, a moderately basic anion exchange resin and a weakly basic anion exchange resin, and a porous resin having both of a weakly basic group and a weakly acidic group. Among these resins, preferred resins are a strongly basic anion exchange resin and a Cl type porous anion exchange resin.

As the decolorization resin, commercially available anion exchange resins may be used. Examples of the commercially available resins are, for example, DOWEX (the registered trademark for a product of The Dow Chemical Company) MAS-1, SBR-P, 11 and 66 DUOLITE (the registered trademark for a product of Diamond Shamrock Company) A-30, A-40LC, A-42LC, A-43, A-101 and A-102, and AMBERLITE (the registered trademark for a product of Rhom & Haas Co.) IRA-401, IRA-402 and IRA-411.

The most preferred decolorization resin is one derived from a macroporous copolymer of a monovinyl aromatic monomer and a crosslinking monomer, where the macroporous copolymer has been post-crosslinked in the swollen state in the presence of a Friedel-Crafts catalyst and functionalized with hydrophilic groups.

The macroporous copolymer is broadly defined to include copolymers prepared by suspension polymerization of a monomer composition under conditions conventionally used to prepare ion exchange resins, in the presence of one or more porogenic diluents using quantities sufficient to cause phase separation of the prepared copolymer from the diluent. Although, it should be noted that there are many other polymerization

techniques known in the art for preparing copolymers which could be useful in polymerization herein.

5 When a macroporous copolymer is contacted with a swelling solvent, such as chloromethyl methyl ether, its structure is characterized by the presence of regions of densely packed polymer chains separated by pores, often referred to as mesopores (50 to 200 Å) and macropores (>200 Å). The nonuniformity of the internal
10 structure of a swollen macroporous copolymer causes the copolymer to appear opaque because of its ability to refract light. If inert diluents or swelling solvents are removed from the macroporous copolymer, for example by subjecting the copolymer to vacuum or steam
15 distillation, then in many instances the pores will collapse from the stress of internal pressures created by increased attractive forces among the regions of packed polymer chains, and the copolymer would then appear transparent or translucent. A class of
20 macroporous copolymers has been developed which retains its porous structure even upon removal of inert diluents or swelling solvents. Such macroporous copolymers are referred to as "macroreticular" copolymers and are
25 described in U.S. Patent 4,382,124. They are characterized by their opaque appearance, regardless of whether or not the copolymer is examined in the presence or absence of inert diluents or swelling solvents.

30 Processes for preparing macroreticular copolymers of a monovinyl aromatic monomer and a crosslinking monomer, which have been post-crosslinked with a polyfunctional alkylating or acylating compound in a swollen state in the presence of a Friedel-Crafts
35 catalyst, are disclosed in U.S. Patents 4,191,813 and 4,263,407, herein incorporated by reference. Such

macroreticular copolymers are referred to as "macronet polymeric adsorbents". A macronet polymeric adsorbent can be functionalized with hydrophilic groups using conventional methods for functionalizing copolymers which are prepared via suspension polymerization with ion exchange groups. For example, the polymeric adsorbent can be functionalized by aminating a chloromethylated polymeric adsorbent with either a dimethylamine, trimethylamine, or dimethylethanolamine, depending on whether weak base or strong base functionality is desired. Similarly, the macronet polymeric adsorbent can be functionalized by sulfonation. Alternatively, a chloromethylated polymeric adsorbent can be functionalized by solvolysis at elevated temperatures.

The most preferred process for preparing decolorization resins which have been post-crosslinked in a swollen state in the presence of a Friedel-Crafts catalyst is described in East German Patent DD 249,274 A1. This patent describes post-crosslinking a "solvent-free", chloromethylated macroporous copolymer of styrene and divinylbenzene. After chloromethylation, the copolymer is first contacted with a washing agent, such as methanol, and then the washing agent is removed by either drying the washed copolymer or extracting the washing agent with the swelling solvent used for the subsequent post-crosslinking reaction. After post-crosslinking the chloromethylated copolymer, the copolymer can be functionalized with hydrophilic groups in the conventional manner, thereby producing a useful adsorbent resin. If it is desirable, functionalization could also be performed before post-crosslinking the copolymer.

Although the East German patent only describes a process for preparing decolorization resins from macroporous copolymers of styrene and divinylbenzene, the process can be used to prepare other macroporous copolymers of a monovinyl aromatic monomer and a crosslinking monomer. These copolymers can be used to produce other adsorbent resins which can be employed to decolorize aqueous sugar solutions.

Regardless of the method used for functionalizing the post-crosslinked macroporous copolymer, after functionalization, the decolorization resin's hydrophilic character increases its efficiency to adsorb color bodies from sugar solutions and desorption of those color bodies from the resin. Desorption can be accomplished with an aqueous base or an organic solvent, such as ethanol. Preferably, the macroporous copolymer is functionalized by first chloromethylating the copolymer, post-crosslinking the copolymer and then aminating the chloromethylated post-crosslinked copolymer with dimethylamine, trimethylamine or dimethylethanolamine. Most preferably, the post-crosslinked macroporous copolymer is functionalized by aminating the chloromethylated copolymer with dimethylamine. Using conventional ion exchange terminology, an adsorbent resin functionalized in this manner and then contacted with an acidic solution is thus converted to its acid form, which is the form desired for decolorizing many aqueous sugar solutions.

Preferred monovinyl aromatic monomers are styrene and its derivatives, such as α -methylstyrene and vinyl toluene; vinyl naphthalene; vinylbenzyl chloride and vinylbenzyl alcohol. Crosslinking monomers broadly

encompass the polyvinylidene compounds listed in U.S. Patent 4,382,124. Preferred crosslinking monomers are divinylbenzene (commercially available divinylbenzene containing less than 45 weight percent
5 ethylvinylbenzene), trivinylbenzene, and ethylene glycol diacrylate.

The preferred macroporous copolymer is a copolymer of up to 99.75 weight percent styrene with the
10 balance divinylbenzene. Another preferred macroporous copolymer is a copolymer of 40 to 60 weight percent styrene, 40 to 60 weight percent vinylbenzyl chloride and 1 to 20 weight percent divinylbenzene. The
15 macroporous copolymers may contain minor amounts of other monomers, such as the esters of acrylic and methacrylic acid, and acrylonitrile.

The crosslinker serves to increase the physical stability of the adsorbent resin. The amount of
20 crosslinker required depends significantly on the process conditions used to prepare the copolymer and can range anywhere from 1 to 45 percent by weight of total monomer, preferably from 4 to 8 percent by weight.

25 Post-crosslinking in a swollen state displaces and rearranges polymer chains, causing an increase in the number of micropores ($<50\text{\AA}$ diameter) and mesopores. This increases porosity and surface area and decreases
30 average pore size. Just as significantly, post-crosslinking also imparts rigidity to the polymer, which reduces its tendency to shrink or swell upon contact with an aqueous solution (often referred to in the ion exchange art as the "shrink/swell") and reduces
35 its dry weight capacity when functionalized, which is an indication of its ion exchange capacity. These

properties as characterized above increase the capacity of the adsorbent resin to adsorb color bodies, increase its permeability to sugar solutions, and increase its physical and dimensional stability.

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Furthermore, the reduced shrink/swell and dry weight capacity of the adsorbent resin, which post-crosslinking induces, is conducive to simple, inexpensive and efficient regeneration once color bodies are loaded onto the resin. The reduced dry weight capacity allows desorption of color bodies from the loaded resin with a dilute base. Concentrated bases or acids are unnecessary for regeneration or cleaning. The reduced shrink/swell property allows the resin to maintain sufficient porosity to minimize entrapment of color bodies, and this property in combination with the reduced dry weight capacity reduces the tendency of the resin to retain color bodies during regeneration.

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The amount of post-crosslinking required for any given application is an amount effective to achieve the adsorbent resin properties described above to the extent desired.

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The decolorization resin preferably has a surface area of 150 to 2100 square meters per gram of dry adsorbent resin (m^2/g), more preferably 700 to 1400 m^2/g . Surface area is measured by BET nitrogen adsorption techniques. Porosity ranges from 0.10 to 0.70 cubic centimeters of pore volume per cubic centimeter of resin (cc/cc), preferably 0.43 to 0.58 cc/cc , as calculated from BET nitrogen adsorption techniques. The porosity contributed by micropores ranges from 30 to 100 percent, preferably 30 to 50 percent, depending on the resin characteristics.

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Percent shrink/swell ranges below 15 percent, more preferably below 7 percent, and most preferably below 4 percent. Percent shrink/swell is determined by measuring the volume expansion or contraction of the adsorbent resin when subjected to hydration or a change in ionic form. The dry weight capacity, determined according to conventional methods used for characterizing ion exchange resins, ranges from greater than zero to 4.0 milliequivalent per gram (meq/g), preferably from greater than zero to 2.0 meq/g. If the macroporous copolymer is functionalized by solvolysis, for example by contact with water or an alcohol, then the dry weight capacity is essentially zero.

The decolorization resin can be used in the form of beads, pellets or any other form desirable for decolorizing aqueous sugar solutions. If the decolorization resin is used in the form of beads, bead size ranges from 10 to 100 microns (μ), preferably from 100 to 800 μ , and more preferably from 300 to 800 μ .

The decolorization resin and the sugar solution may be contacted using conventional methods which result in intimate contact between the resin and the sugar solution. Suitable methods include fluidized beds, stirred tanks, batch tanks, and cocurrent and countercurrent flow columns. The contacting may occur batchwise, semi-batchwise, continuously or semi-continuously. Preferably, the solution is contacted with the resin continuously in a packed column.

The residence time required for contact between the decolorization resin and the sugar solution depends on the following: (1) the properties of the resin, (2) the amount of color bodies initially present,

(3) the level of decolorization desired, (4) the amount of resin used, (5) the viscosity of the sugar solution, (6) the concentration of dissolved sugar (often referred to as dissolved solids), (7) the processing temperature, and (8) the pH of the sugar solution. Therefore, the residence time must be determined empirically. Preferably, the residence time ranges from 0.1 hours (10 bed volumes/hr) to 10 hours (0.1 bed volumes/hr), more preferably 0.12 hours (8 bed volumes/hr) to 1 hour (1 bed volume/hr), and most preferably 0.17 hours (6 bed volumes/hr) to 0.5 hours (2 bed volumes/hr).

The temperature should remain below the temperature at which the sugar solution is adversely affected. Generally, temperatures ranging from 20°C to 80°C are operable. Preferably, the temperature ranges between 38°C and 55°C.

The amount of decolorization resin required, largely depends on equipment configuration, concentration of dissolved solids, the level and type of color bodies present, and the level of decolorization desired.

In the present invention, the sugar solution decolorized with the above-mentioned decolorization resin is subjected to a decationization treatment with a cation ion exchange resin such as DOWEX™ HCR-W2, and then to a deanionization treatment with an anion exchange resin such as DOWEX™ 66. If desired, the sugar solution is subjected to an anion exchange treatment packed with a mixture of a cation exchange and an anion exchange resin.

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In a preferred embodiment of the present invention, the decolorization treatment and the decationization treatment are carried out in one column in which the decolorization resin is packed in the upper layer portion and the cation exchange resin is packed in the lower layer portion. Where this column is used, the conduit equipment and space area can be reduced and the process becomes industrially advantageous. Furthermore, where a resin-regenerating liquid discharge opening is arranged at the intermediate portion of this column, the decolorization resin and cation exchange resin can be efficiently regenerated by introducing a regenerating liquid from the upper and lower portions of the column.

Examples of aqueous sugar solutions that are advantageously treated according to the present invention include carbohydrate solutions derived from corn starch, such as corn syrup, high fructose corn syrup, dextrose, and sorbitol; sucrose, beet and cane sugar, palm sugar, maple sugar; fruit juices, either natural or processed, such as pear, apple, grape and pineapple mill juices; sugar solutions derived from sorghum; and high fructose syrups derived from tapioca, insulin and potato starch. Preferably, the sugar solution is a solution of corn syrup, high fructose corn syrup, sorbitol, sucrose or dextrose.

The present invention is further described by the following examples and comparative examples.

Example 1

An unpurified aqueous solution of glucose (BX = 30, pH = 7.2, electroconductivity = 582 μ s/cm) was introduced at a space velocity of 4 into a column packed

with 50 ml of a Cl type strongly basic anion exchange resin (DOWEX™MSA-1) as the decolorization weak acid removal resin. The weak acid removing capacity (based on the ion exchange capacity) and the decolorizing capacity (based on the absorbance) were evaluated with respect to the discharge liquid. The results are shown in Table 1. The discharged decolorized glucose solution was passed through a column packed with 50 ml of a hydrogen-type strongly acidic cation exchange resin (DOWEX™ HCR-W2) to effect a decationization treatment, and the liquid was passed through a column packed with 50 ml of an anion exchange resin (DOWEX™ 66) to effect a deanionization treatment. During this treatment, the electroconductivity of the discharged glucose solution was continuously measured. The results are shown in Figure 1. Similarly, at the point at which the electroconductivity was lowest during the ion exchange purification, the absorbance of the discharged liquid was measured. The results are shown in Table 2.

Example 2

An aqueous solution of glucose was purified in the same manner as described in Example 1 except that 50 ml of a weakly basic anion exchange resin (DOWEX™ 66) was used as the decolorizing resin, and the evaluation was carried out in the same manner as described in Example 1.

Comparative Example 1

An aqueous solution of glucose was purified in the same manner as described in Example 1 except that active carbon was used instead of the decolorization

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resin, and the evaluation was carried out in the same manner as described in Example 1.

Comparative Example 2

5 An aqueous solution of glucose was purified in the same manner as described in Example 1 except that the decolorization resin and active carbon were not used, i.e., the decolorizing step was omitted, and the
10 evaluation was carried out in the same manner as described in Example 1.

Table 1

15	Ion Exchange Capacity (meq/ml)	Example	Example	Comparative	Comparative
		1	2	Example 1	Example 2
	strong acid	0.0132	0.0112	0.0119	0.0123
	weak acid	0.0024	0.0027	0.0042	0.0041

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Table 2

25	Absorbance (wavelength)	Example	Example	Comparative	Comparative
		1	2	Example 1	Example 2
	420 nm	0.063	0.072	0.227	0.378
	280 nm	0.1201	0.1437	0.972	1.060

30 From the results shown in the Tables and in Figure 1, it is seen that, according to the present invention, much higher decolorizing and salt-removing effects can be obtained than those obtained by the conventional processes, and the treatment capacity can be increased.

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Example 3

5 An aqueous solution of glucose was purified in the same manner as described in Example 1 except that a resin column packed with 50 ml of a decolorization resin (DOWEX™ MSA-1) at the upper layer portion and 50 ml of a cation exchange resin (DOWEX™ HCR-W2) at the lower layer portion was used, and the evaluation was carried out in the same manner as described in Example 1. The
10 same effects were obtained as in Example 1.

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CLAIMS

1. A process for purifying a sugar solution using cation exchange resin and an anion exchange resin, which comprises contacting a sugar solution with a decolorization resin to remove color bodies and weakly acidic substances prior to the decationization by the cation exchange resin.

2. The process of Claim 1, wherein the decolorization resin is an anion exchange resin or a porous resin having both of a weakly basic group and a weakly acidic group.

3. The process of Claim 2, wherein the anion exchange resin is a strongly basic anion exchange resin, a moderately basic anion exchange resin, a weakly basic anion exchange resin or a Cl type porous anion exchange resin.

4. The process of Claim 1, wherein the decolorization resin is derived from a macroporous copolymer of a monovinyl aromatic monomer and a crosslinking monomer, where the macroporous copolymer has been post-crosslinked in the swollen state in the presence of a Friedel-Crafts catalyst and functionalized with hydrophilic groups.

5. The process of Claim 4, wherein the crosslinking monomer is a polyvinylidene monomer.

5 6. The process of Claim 5, wherein the polyvinylidene monomer is divinylbenzene, trivinylbenzene or ethylene glycol diacrylate.

10 7. The process of Claim 6, wherein the monovinyl aromatic monomer is styrene or a derivative of styrene, vinyltoluene, vinylbenzyl chloride, vinylbenzyl alcohol or vinylnaphthalene.

8. The process of Claim 4, wherein the macroporous copolymer is chloromethylated.

15 9. The process of Claim 4, wherein the macroporous copolymer is post-crosslinked with a polyfunctional alkylating or acylating compound.

20 10. The process of Claim 4, wherein the post-crosslinked macroporous copolymer is functionalized with dimethylamine, trimethylamine or dimethylethanolamine.

25 11. The process of Claim 4, wherein the decolorization resin has a surface area of 150 to 2100 m²/g.

30 12. The process of Claim 4, wherein the decolorization resin has a porosity of 0.10 to 0.70 cc/cc.

35 13. The process of Claim 4, wherein the decolorization resin exhibits a percent shrink/swell below 7 percent.

14. The process of Claim 4, wherein the dry weight capacity of the decolorization resin ranges from greater than zero to 4.0 meq/g.

5 15. The process of Claim 1, wherein the decolorization, weakly acidic substance-removal and decationization are carried out with a column filled with the decolorization at the upper layer portion and with the cation exchange resin at the lower layer
10 portion.

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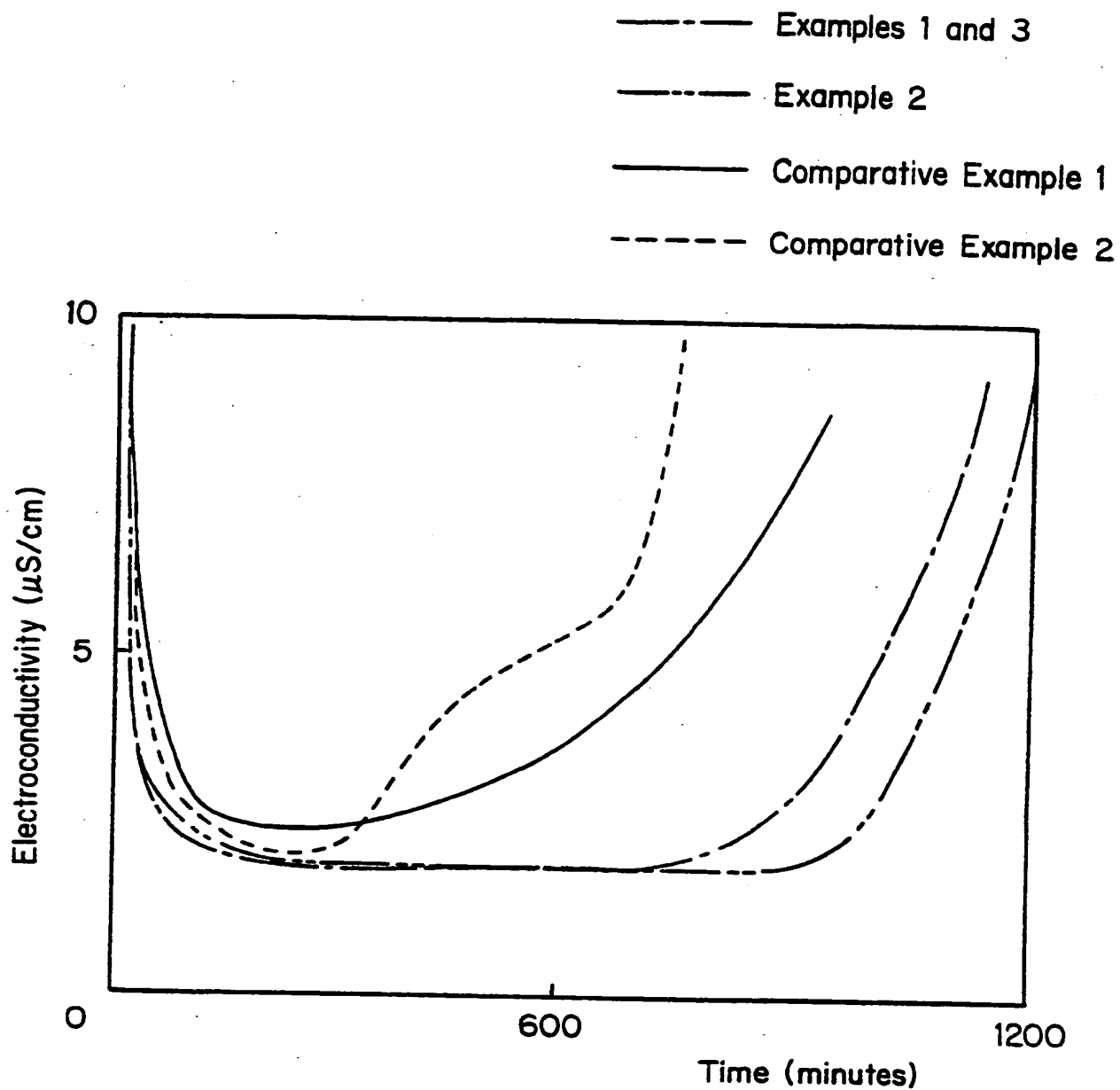


FIG. 1

SUBSTITUTE SHEET

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INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/03793

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL. ⁴	C13D, 3/14; C13D, 3/12	**685,681
U.S. CL.	127/46.2, 46.3, 55; 502/159; 521/30, 33, 29; 426/271; 210/660,	
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
U.S.	127/46.2, 46.3, 55; 502/159; 521/30, 33, 29; 426/271; 210/660, 685, 681	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	US, A, 2,828,270, (Murata et al), 25 March 1958, See column 1, lines 65-70 and column 5, lines 50-58	1-3
Y	US, A, 4,191,813, (Reed et al), 04 March 1980, See the entire document	1-15
Y	US, A, 4,263,407, (Reed, Jr.), 21 April 1981, See the entire document	1-15
Y	US, A, 4,382,124, (Meitzner et al), 03 May 1983, See the entire document	1-15
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Δ" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
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